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SYNTHESIS AND PROPERTIES OF ACRYLATE NANOCOMPOSITES

FINAL REPORT

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PMMA Nanocomposites Synthesized by Emulsion Polymerization

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Well-dispersed (exfoliated) PMMA nanocomposites were synthesized via emulsion polymerization. The nanocomposites retain their transparency in the visible with the montmorillonite nanocomposite showing considerable absorption of UV light. Thermal stability of the nanocomposites is enhanced as evidenced by TGA and a simple burning experiment. The storage modulus and Tg is increased significantly in the nanocomposites. The higher increase of the storage modulus in the rubbery regime of the montmorillonite nanocomposite reflects the higher amount of bound polymer compared to the fluorohectorite nanocomposite. End-tethering of PMMA to the silicate surface increases the amount of bound polymer and results in increases in both Tg and modulus in the rubbery plateau.

Nanocomposites based on layered inorganics offer an alternative to conventionally filled polymers and composites. Due to their nanometer phase dimensions the nanocomposites exhibit new and improved properties. These include increased stiffness and strength without sacrificing impact resistance, decreased permeability and swelling in solvents, and increased flame resistance. For example, nylon nanocomposites show a significant increase in modulus and strength as well as heat distortion temperature. (1,2). Tensile strength and modulus have also been reported to increase considerably in epoxy and polyurethane nanocomposites (2-8). Additionally improved barrier properties (9, 10) and swelling in solvents (11) have been reported for several nanocomposite

systems. Finally the nanocomposites exhibit increased thermal stability and flame resistance (12-15).

Currently, two synthetic approaches have been adopted. One is based on in-situ polymerization of monomers inside the galleries of the inorganic host. (16-20). The other approach is based on melt intercalation of high molecular weight polymers and it involves annealing a mixture of the polymer and the inorganic host, statically or under shear, above the T_g of the polymer (21-24). The solventless melt intercalation is an environmentally friendly technique and is adoptable to existing processing like roll milling, extrusion and molding.

In the present chapter, we report the synthesis of PMMA nanocomposites by emulsion polymerization. Polymerization of MMA in the presence of smectite silicates has been previously reported (25-28). The focus of all these studies, however, was on how the silicates affect the polymerization reaction rather than the final hybrid product. Additionally, the development of an emulsion route to nanocomposites represents a new venue.

Experimental

5 ml of MMA (Sigma Chemicals) was added to a round bottom flask containing 95 ml of water (the ratio of monomer to water is approximately 1:19) followed by 0.25 g of silicate (Na⁺ montmorillonite, hereafter abbreviated as MMT, or fluorohectorite, FH). The resulting suspension was heated at 80°C with stirring and allowed to equilibrate for 2 hrs. An emulsifier is added to allow the reaction to proceed as emulsion polymerization. 0.0125 g of potassium persulfate is added to initiate the polymerization and the suspension is refluxed at 80°C for 4 hrs.. The emulsion is completely precipitated in excess ethyl alcohol. The precipitate is then filtered and re-precipitated from tetrahydrofuran, washed thoroughly with de-ionized water, filtered and dried under vacuum at 80°C. In one particular case the MMT was modified with 2,2' Azobis(2-methylpropionamide) dihydrochloride, hereafter referred to as AMMT.

Table 1: Summary of PMMA and PMMA Nanocomposites Properties

	PMMA	PMMA-MMT	PMMA-FH
Polydispersity index, D	3.49	2.57	2.59
Molecular Weight (g/mol) X 10 ³	195.2	221.7	223.0
Glass Transition Temp. T _g , (°C)	115	121	125
Storage Modulus @ RT (GPa)	2.9	9.9	9.3

MMT: montmorillonite

FH: fluorohectorite

X-Ray diffraction was performed using a Scintag PAD X Diffractometer using Cu-K α radiation. The accelerating voltage used was 45kV

and the current was 40mA. The TEM samples were examined using JEOL 1200EX transmission electron microscope with an accelerating voltage of 120kV. Samples of 0.2 μm to 0.3 μm thickness were cut using a glass knife Reichert Ultramicrotome and mounted on 400 mesh Gilder gold grid. Thermal degradation was followed by a Perkin Elmer System 7, Thermogravimetric Analyzer. Scans were performed from room temperature to 800 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$. For dynamic mechanical analysis a Seiko Instrument, SDM 5200, DMS 200 series was used. The samples were scanned from room temperature to 150 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C}/\text{min}$ at 5Hz and a strain of 0.1%. Absorbance was measured between 200nm and 900nm at a spectral bandwidth of 1 nm and a scan speed of 30nm/sec on a Perkin Elmer spectrophotometer.

Results and Discussion

TEM micrographs of the nanocomposites prepared via emulsion show a well dispersed (exfoliated) sample (Fig. 1). The dispersion is somewhat better in the MMT nanocomposite and is most likely due to the much smaller lateral dimensions of MMT compared to FH. The silicate exfoliation is supported by the featureless XRD patterns of the nanocomposites. Table 1 summarizes the molecular weight and the polydispersity of the polymers for all samples prepared by emulsion polymerization. The nanocomposites show slightly

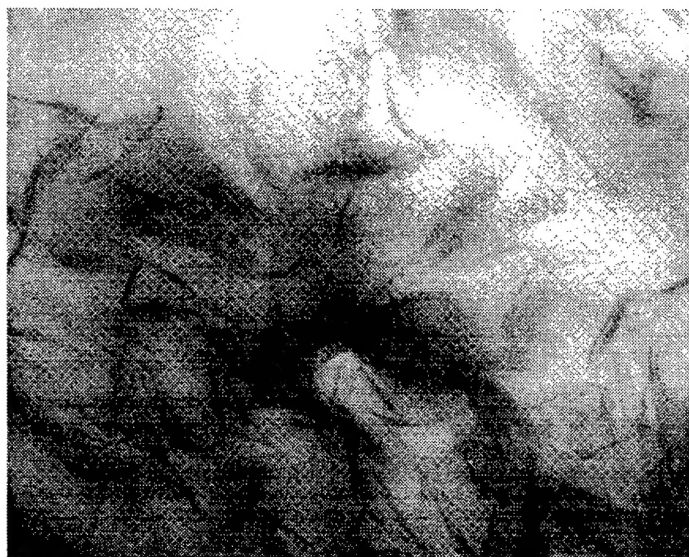


Figure 1: Transmission electron microscope image showing the disordered silicate (montmorillonite) in the PMMA matrix.

higher molecular weights but much better polydispersity than pure PMMA prepared similarly but in the absence of the silicate. Though the mechanism is still unknown, clearly the presence of silicate effects the polymerization reaction.

Clarity of the samples is very important as PMMA is often used in many applications for its transparency. Films were deposited on clean glass substrates by spin casting a suspension of the nanocomposites in tetrahydrofuran, THF. For comparison a PMMA film was prepared by spin casting a solution of PMMA also in THF. The nanocomposites have somewhat higher absorbance compared to the pure polymer, but the absorbance is well below the limit for transparency. Especially in the case of MMT nanocomposite the sample shows increased absorption in the UV. Thus the nanocomposites combine UV absorption while retaining transparency in the visible.

An important characteristic of polymers is their stability at elevated temperatures. Figure 2 and 3 shows the TGA traces of the pure polymer and the nanocomposites in either nitrogen or oxygen. Thermal degradation of PMMA in nitrogen proceeds in three distinctive steps. The first (low temperature) is due to decomposition of relatively weak head-to-head linkages, the second to chain-end decomposition and the third to random scission within the polymer chain (29). In the present case degradation of PMMA in nitrogen (Fig. 2) follows a two-step process (the first step is absent). The onset of the two steps is at 322 and 380 °C, respectively. The FH nanocomposite appears to decompose also in two steps. The derivative shows that the extent of the two steps is reversed from the corresponding PMMA sample. At the same time, the second peak moves to a slightly higher temperature. In contrast, decomposition of the MMT nanocomposite follows a single step suggesting that only decomposition by random scission takes place.

In contrast to nitrogen, oxygen suppresses the degradation of weak linkages at low temperatures but it enhances the degradation via random scission at higher temperatures for the pure PMMA. Similarly to the pure polymer the nanocomposites show one major decomposition step (Fig. 3). The onset decomposition of FH nanocomposite, however, commences a little earlier but it extends to somewhat higher temperatures than the pure PMMA. In contrast, MMT nanocomposites show a large suppression of decomposition compared to the pure polymer with the decomposition temperature increasing by about 50 °C.

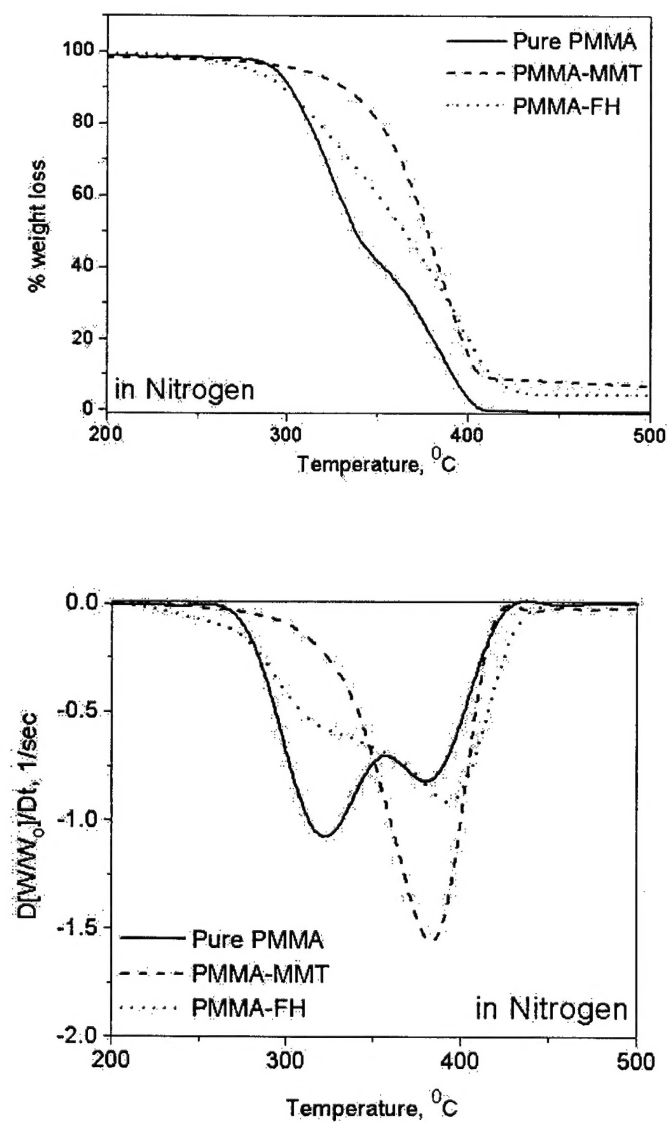


Figure 2: Thermogravimetric traces of the different PMMA nanocomposites in nitrogen.

There are clearly differences between the two nanocomposites and the pure polymer. In addition, the thermal stability depends, if air or nitrogen is used. We are currently attempting to understand and delineate the factors contributing to this behavior. Nevertheless, the thermal stability of the polymer appears to increase in the nanocomposites. The above conclusion is corroborated by a simple burning test using a propane torch. PMMA burns out completely with significant dripping. In contrast, the nanocomposites experience no dripping during burning. Furthermore, the MMT nanocomposite self-extinguishes shortly after the flame is removed. The FH nanocomposite continues to burn but it forms a significant amount of char, which is characteristic of higher thermal stability.

Solomon et al. has observed that clay minerals act as inhibitor for free radical polymerization specifically for PMMA (30). The clay minerals inhibit the free radical reactions by preferential absorption of the propagating or initiating radicals by the Lewis acids and then the reaction either gets terminated by dimerization or disproportionation or by formation of a carbonium ion by electron transfer from the radical to the Lewis acid site. The clay minerals usually made of aluminosilicates and minerals containing higher amount of aluminosilicates are more effective inhibitors. In the present case, MMT is an aluminosilicate while FH contains Mg in the octahedral layer (31). Thus, MMT contains Lewis acid sites but not FH. This might explain the different behavior between the two silicates, MMT and FH, in the nanocomposites. Recently, Gilman et.al. (32) also observed a difference in the flammability behavior of MMT and FH based nanocomposites. They reported that silicate layers reassemble into a multilayer char after the polymer burns away. The smaller MMT plates could reassemble easier compared to the larger size FH leading to differences in the thermal stability between the two nanocomposites.

Finally dynamic mechanical analysis was used to measure the viscoelastic properties of the nanocomposites as a function of temperature. In this measurement the in-phase and out-of-phase components of the stress are measured while a sinusoidal strain is applied to the sample. From the in-phase and out-of-phase components the storage (E') and loss modulus (E''), respectively, can be calculated. The ratio $E''/E' = \tan\delta$ is a measure of the energy lost to energy stored per cycle of deformation and has a maximum at thermal transitions. The DMA measurements of storage modulus, E' , vs. temperature obtained for MMT and FH nanocomposites and pure PMMA are shown in Figure 4. An increase in T_g is evident for both MMT- and FH nanocomposites. In addition, the DMA data revealed an-order-of-magnitude in the rubbery plateau modulus for the MMT nanocomposite compared to the pure PMMA.

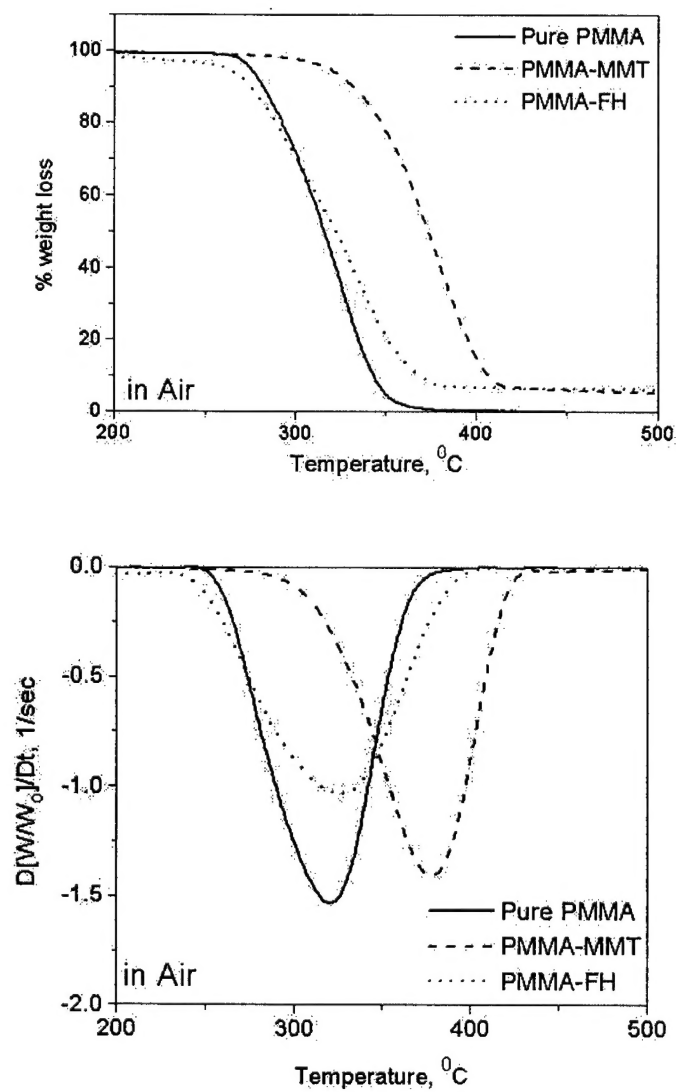


Figure 3: Thermogravimetric traces of the different PMMA nanocomposites in air.

Interestingly, the increase in the rubbery plateau modulus is more significant in the MMT- than that in FH-based nanocomposite. This trend might reflect the differences in the amount of strongly interacting polymer (bound polymer) for the two nanocomposites. After extraction in chloroform at room temperature MMT retains 40 % polymer while only 7 % is left in FH. The much higher amount of bound polymer in MMT might act as potential crosslinks increasing the rubbery modulus to a greater extent.

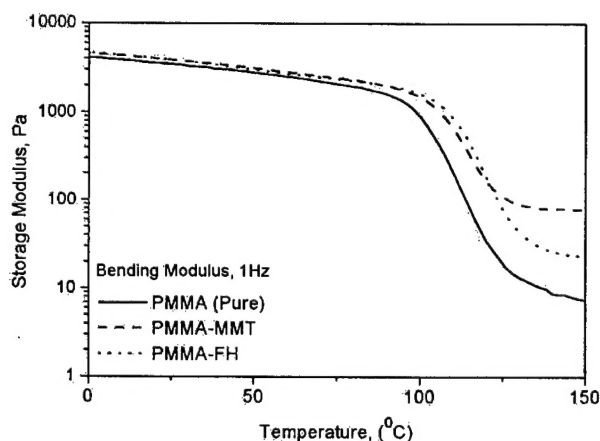


Figure 4: Dynamic mechanical analysis plots for the different PMMA nanocomposites

Table 2 contrasts the properties of MMT nanocomposites prepared by emulsion polymerization (PMMT) to those obtained by dispersion polymerization of AMMT-exchanged MMT (P50). Since the initiator is tethered to the silicate surface in the latter a significant amount of the PMMA chains are also tethered to the clay surface. The silent XRD corresponds to well-dispersed (exfoliated) nanocomposites. Both T_g and modulus in the rubbery plateau are higher from the corresponding nanocomposites prepared via emulsion polymerization. This probably reflects the amount of bound polymer being higher (82 vs. 40%) when AMMT is used as an initiator resulting in surface tethered PMMA chains.

Table 2: Summary of Properties for Nanocomposites and PMMA

Sample	XRD Initial, nm	XRD Final, nm	DMA, T _g °C	Bound Polymer
Pure	--	-	109	--
PMMT	11.1	Silent	122	40%
P50	12.1	Silent	126	82%

PMMT: nanocomposites prepared by emulsion polymerization

P50: nanocomposites prepared by dispersion polymerization of AMMT-exchanged MMT

Conclusion

The synthesis of well-dispersed (exfoliated) PMMA nanocomposites via emulsion polymerization is described. The nanocomposites retain their transparency in the visible with the MMT nanocomposite showing considerable absorption of UV light. Thermal stability of the nanocomposites is enhanced as evidenced by TGA and a simple burning experiment. The storage modulus and T_g is increased significantly in the nanocomposites. The higher increase of the storage modulus in the rubbery regime of the MMT nanocomposite reflects the higher amount of bound polymer compared to the FH nanocomposite. End-tethering of PMMA to the silicate surface increases the amount of bound polymer and results in increases in both T_g and modulus in the rubbery plateau.

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